Micellar impact on Ternary complexes of essential metal ions with selective bio-ligands

[1]**Srinivasa Rao Pedada**, [2]**Nageswara Rao Gollapalli**

[1]Assistant professor, Gayatri vidya parishad engineering college for women Visakhapatnam-530 048, India
[2]Professor, School of Chemistry, Andhra University, Visakhapatnam-530 003, India.

***ABSTRACT*: Chemical speciation of ternary complexes of L-aspartic and citric acids with essential metals like Co(II), Ni(II), Cu(II) and Zn(II) solutions containing different ratios (1:2:2, 1:2:4 and 1:4:2) of metal to primary (L) to secondary ligands (X) has been investigated in surfactant-water mixture (SLS). The stability constants of ternary complexes are refined using the computer program MINIQUAD75. The ternary complexes detected are MLX, MLXH and MLX$_2$H. The variation of stability constants with mole fraction of the surfactant is explained on the basis of electrostatic and non-electrostatic forces. The distribution diagrams indicate that ternary species are more predominant than the binary species. The extra stability associated with the ternary complexes is attributed to factors such as charge neutralization, chelate effect, stacking interactions and hydrogen bonding.**

Index terms- L-aspartic acid, Citric Acid, Essential metals, Speciation, Ternary Complexes

1. INTRODUCTION

A scrupulous study of all the species existing in every system is impossible due to limitations of the available experimental methods. Hence modeling studies involving ternary complexes have gained popularity. Ternary complexes containing a metal ion and two different ligands have been studied previously [1-3]. Ternary complex equilibria of L-arginine, L-histidine [4] oxalic and malonic acids [5] and [6] L-glutamic acid and L-ornithine [7] were reported earlier in miceller media. The protonation and binary complexes of L-aspartic, citric and succinic acids with Co(II), Ni(II), Cu(II) and Zn(II) have been reported recently [8-10]. This paper reports a pH metric study of the speciation of ternary complexes of L–aspartic acid (Asp) and citric acid (Cit) with some essential metal ions in cationic (SLS) miceller media of varying compositions.

2. METHODOLOGY

2.1 Apparatus and Chemicals

0.1 Mol dm^{-3} aqueous solutions of Co(II), Ni(II), Cu(II) and Zn(II) chlorides (GR Grade, Merck, India) were prepared in triple distilled water. 0.05 mol dm^{-3} aqueous solutions of Asp (E-Merck, Germany) and Cit (Merck GR, India) were also prepared. To increase the solubility of the ligands, 0.05 mol dm^{-3} nitric acid concentration was maintained in the solutions. GR sample of Sodium laurylsulphate (SLS, Qualigens, India.) was used and their purity was checked by determining critical micellar concentration (CMC) conductometrically. The CMC value of SLS was 8.1 X10^{-3}, at 303K. The strength of alkali was determined using the Gran plot [11] method. The errors in the concentrations of ligand, metal ions and alkali were subjected to analysis of variance (ANOVA) [12]

2.2 Experimental Method

The titrations were carried out in the medium containing varying concentrations of surfactant (0.0-2.5% w/v) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium nitrate at 303.0±0.1 K. The measurements were recorded with an ELICO (Model LI-120) pH meter of readability 0.01 in conjunction with a glass and calomel electrode. The glass electrode was equilibrated in a well stirred surfactant-water mixture containing inert electrolyte. The effect of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode are accounted for in the form of correction factor [13] which was computed from the experimental and simulated acid-base titration data calculated by SCPHD program [14]. A correction was applied to the pH meter dial readings to account for the solvent effect on pH.

Titrations were carried out in presence of different relative concentrations (Table 1) of metal (M) to Asp (L) and Cit (X) (M: L: X = 1:2:2, 1:2:4, 1:4:2) with 0.4 mol dm^{-3} NaOH. The details of experimental procedure and titration assembly are given elsewhere [15]. The best-fit chemical model for each system investigated was arrived at using non-linear squares analysis using MINIQUAD[16] which exploits the advantage of constrained least squares method in the initial refinement and reliable convergence of undamped and unconstrained Marquardt algorithm. Different models containing varied number of ternary species were generated using the expert systems CEES [17].

3. RESULT AND DISCUSSION

The alkalimetric titration data of mixtures containing different mole ratios of Asp and Cit inferred that these two ligands do not form any condensed species [18]. Assuming that Asp and Cit are tridentate ligands the total number of primary (L) and

secondary ligands (X) together was restricted to a maximum of three in generating the possible ternary species. The possible primary and secondary ligands forms resultant ternary complex species are shown in Table 2.

3.1 *Selection of Best Fit Model*

The formation constants for acido-basic equilibria of both primary and secondary ligands and those for binary metal complexes were fixed in testing various chemical models using the computer program MINIQUAD75. The best fit model was chosen as that with low standard deviation in the formation constants and minimum sum of the squares of residuals U (corrected for degree of freedom) which was corroborated by other statistical parameters like χ^2, R-Factor etc. which are given in Table. 3

3.2 *Effect of Micelles*

The variation of the stability constants with mole fraction of the surfactant (SLS) is shown in Figure 1. The non-linear decrease in the stability of ternary complexes with mole fraction of the surfactant indicates the dominance of non-electrostatic forces over electrostatic forces and decreased dielectric constant with increased surfactant concentration. The species should be stabilized in the micellar medium with opposite charges due to electrostatic interactions but these charged species should be destabilized [19] due to the decreased dielectric constant of the medium and due to the stabilization of the species, causes stacking interactions between NH_3^+ of one ligand with the oxygen dipole of the neighboring ligand. The reason [20] for the extra stability of ternary complexes may be due to interactions outside the coordination sphere such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect and stacking interactions.

3.3 *Distribution Diagrams*

In the pH range of the present study, L-aspartic acid (2.0-11.0) exists as LH_3, LH_2^-, LH^{2-} and L^{3-} while citric acid (1.7-8.0) exists as XH_3, XH_2^-, XH^{2-} and X^{3-} respectively [21, 22] . These ligands interact with the metal ions to form MLX^{3-}, $MLXH^{2-}$ and MLX_2H^{5-} species. Here, L is Asp and X is Cit. Some typical distribution diagrams of these species are given Figure 2. The species MLX^{3-} exists in the pH range 6.0–8.0, for Co(II), Ni(II), Cu(II) and Zn(II), where as $MLXH^{2-}$, exists in the pH range of 6.0-8.0 for Cu(II) and Zn(II), 2.0-4.0. for Ni(II) and 4.0-5.50 for Co(II) and MLX_2H^{5-} exists at 6.0-8.0 for all the metals. The formation of the complex species can be represented by the following equilibria. The species MLX^{3-} in the pH region 6.0-9.0 can be represented by the following equilibria:

1) $M(II) + LH^- + XH^{2-} \leftrightarrow MLX^{3-} + 2H^+$
2) $M(II) + LH_2 + XH_2^- \leftrightarrow MLX^{3-} + 4H^+$
3) $M(II) + LH_3^+ + XH_3 \leftrightarrow MLX^{3-} + 6H^+$

$MLXH^{2-}$ might have formed due to some of the following equilibria in the pH range 2.0-8.0.

4) $M(II) + LH_3^+ + XH^{2-} \leftrightarrow MLXH^{2-} + 3H^+$
5) $M(II) + LH_2 + XH_3 \leftrightarrow MLXH^{2-} + 4H^+$
6) $M(II) + LH^- + XH_2^{2-} \leftrightarrow MLXH^{2-} + 2H^+$

The species MLX_2H^{5-} formed; in the pH region 6.0-8.0 can be represented by the following equilibria:

7) $M(II) + LH_3^+ + 2XH_2^- \leftrightarrow MLX_2H^{5-} + 6H^+$
8) $M(II) + LH_2 + 2XH_3 \leftrightarrow MLX_2H^{5-} + 6H^+$
9) $M(II) + LH_2 + 2XH^{2-} \leftrightarrow MLX_2H^{5-} + 3H^+$

REFERENCES

[1] K. V. Lavanya, V. M. Rao, G. N. Rao, *Oxid. Commun.* **2008**, 31, 398-409.
[2] G. N.Rao, K .G. Sudarsan, *Chem. Speciat. Bioavail.* **2006**, 18, 71-76.
[3] G. N. Rao, A. Ramakrishna, *J . Indian Chem. Soc.* **2006**, 83, 332-335.
[4] K. V. Lavanya, K. Y. Kiran Kumar, T. S. Rao, G. N. Rao, *J. Indian Chem . Soc.* **2003**, 80, 783.
[5] B. B. V.Sailaja, T. Kebede, G. N. Rao, M. S. .P. Rao, *Proc. Natl . Acad. Sci. India.* **2004**, 4, 399-412.
[6] B. B. V.Sailaja, T. Kebede, G. N. Rao, M..S. .P. Rao, *J. Indian Chem. Soc.* **2002**, 79, 155-158.
[7] J. Stanley Sukumar, G. N. Rao K. V. Ramana, M. S. P. Rao, *Indian J. Chem.* **1996**, 35A, 121-126.
[8] P. S. Rao, B. Srikanth, V. S. Rao, C. K. Sastry, G. N. Rao, *Bull. Chem. Soc. Ethiopia.* **2009**, 23, 347-358.
[9] B. Srikanth, P. S. Rao, V. S. Rao, C .K. Sastry, G. N. Rao, *Serb. Chem. Soc.* **2009**, 74(X), 745-754.
[10] V. S. Rao, P .S. Rao, B. Srikanth,C. K. Sastry, G. N. Rao, *Chem. Speciat. Bioavail.* **2009**, 12, 72-80.
[11] G. Gran, *Anal. Chim. Acta.* **1988**, 206, 111-123.
[12] R. S. Rao, G. N. Rao, *Computer Applications in Chemistry,* Himalaya Publishing House, Mumbai, India, **2005** .
[13] M. P.Latha, V. M. Rao, T. S. Rao, G. N. Rao, *Bull. Chem. Soc. Ethiopia.* **2007**, 21, 363-372.
[14] G. N. Rao, *Ph.D. Thesis*, Andhra University,Visakhapatnam, India, **1989**.
[15] N. Padmaja, M . S. Babu, G. N. Rao, R. S. Rao, K. V. Ramana, *Polyhedron.* **1990**, 9, 2497-2506.
[16] G. Gans, A. Sabatini, A. Vacca, *Inorg. Chim. Acta.* **1976**, 18, 237-239
[17] A.Braibanti, R. S. Rao, A .R. Babu, G. N.Rao, *Ann. Chim. Italy.* **1995**, 85, 17-29
[18] G. N. Rao, S. B. Ronald, *J .Indian. Chem. Soc.* **2002**,79, 416-419.
[19] V. U. S. Sagar, G. Himabindu, K. G. Sudarsan, G. N. Rao, *J. Indian. Chem. Soc.* **2005**, 82, 598-601.
[20] T. Sakurai, O. Yamauchi, A. Nakahara, *Bull. Chem. Soc. Jpn.* **1977**, 50, 1776-1779.

[21]   P. S. Rao, B. Srikanth, V. S. Rao, C. K. Sastry, G. N. Rao, *E- J. Chem.* **2009**, 6, 561-568.

[22]   B. Srikanth, P. S. Rao, V. S. Rao, C. K. Sastry, G. N. Rao, *Proc. Natl. Acad. Sci . India,* **2009**, 79A(IV), 335-340.

Table 1: Total initial concentrations of ingredients (in mmol) for mixed-ligand titrations in micellar media [NaOH] = 0.4 mol dm^{-3}; V_0 =50.0 cm^3; Temp= 303 K; Ionic strength=0.16 mol dm^{-3}; Mineral acid =1 mmol

% (w/w) Surfactant	TM0				TL0		M:L:X
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Asp	Cit	
0.0	0.107	0.099	0.101	0.097	0.200	0.200	1:2:2
					0.200	0.400	1:2:4
					0.400	0.200	1:4:2
0.5	0.107	0.099	0.101	0.097	0.200	0.200	1:2:2
					0.200	0.400	1:2:4
					0.400	0.200	1:4:2
1.0	0.107	0.099	0.101	0.097	0.200	0.200	1:2:2
					0.200	0.400	1:2:4
					0.400	0.200	1:4:2
1.5	0.107	0.099	0.101	0.097	0.200	0.200	1:2:2
					0.200	0.400	1:2:4
					0.400	0.200	1:4:2
2.0	0.107	0.099	0.101	0.097	0.200	0.200	1:2:2
					0.200	0.400	1:2:4
					0.400	0.200	1:4:2
2.5	0.107	0.099	0.101	0.097	0.200	0.200	1:2:2
					0.200	0.400	1:2:4
					0.400	0.200	1:4:2

Table 2: Some of the possible ternary complex species System: M(II)-Asp and Cit

Constraints: 1. Maximum number of primary ligand = 2

2. Maximum number of secondary ligand = 2

3. Primary+Secondary ligands

	Primary	Secondary	2	3	
1	LH$_3$	XH$_3$	MLXH$_4$	ML$_2$XH$_6$	MLX$_2$H$_6$
2	LH$_3$	XH$_2$	MLXH$_3$	ML$_2$XH$_5$	MLX$_2$H$_4$
3	LH$_3$	XH	MLXH$_2$	ML$_2$XH$_4$	MLX$_2$H$_2$
4	LH$_2$	XH$_3$	MLXH$_3$	ML$_2$XH$_4$	MLX$_2$H$_5$
5	LH$_2$	XH$_2$	MLXH$_2$	ML$_2$XH$_3$	MLX$_2$H$_3$
6	LH$_2$	XH	MLXH	ML$_2$XH$_2$	MLX$_2$H
7	LH	XH$_3$	MLXH$_2$	ML$_2$XH$_2$	MLX$_2$H$_4$
8	LH	XH$_2$	MLXH	ML$_2$XH	MLX$_2$H$_2$
9	LH	XH	MLX	ML$_2$X	MLX$_2$

Table 3: Parameters of best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)-Asp and Cit complexes in SLS-water mixtures

% W/V SLS	Logβ (SD)			NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
	MLX	MLXH	MLX$_2$H							
Co(II)										
0.0	16.97(15)	21.73(25)	27.53(32)	137	8.29	-0.94	101.32	0.0014	5.02	2.00-11.00
0.5	16.50(08)	21.73(16)	27.44(24)	104	2.77	0.19	35.04	0.0243	2.97	2.00-10.50
1.0	16.83(10)	21.02(19)	--	109	9.15	0.22	31.09	0.0373	3.74	2.00-10.50
1.5	17.94(07)	22.04(18)	--	107	9.71	0.97	29.05	0.0543	4.21	2.00-10.50
2.0	17.87(04)	--	28.00(18)	102	1.21	0.11	31.09	0.0714	3.97	2.00-10.30
2.5	17.93(05)	22.54(11)	28.12(30)	100	3.03	0.70	42.04	0.0611	2.83	2.00-10.50
Ni(II)										
0.0	15.63(08)	21.92(19)	27.97(26)	158	9.80	0.85	54.32	0.0811	3.29	2.00-11.50
0.5	15.37(08)	20.73(17)	27.75(32)	93	6.55	-0..92	54.98	0.0784	4.92	2.00-10.50
1.0	15.77(04)	20.84(15)	27.69(35)	90	3.33	-1.02	60.03	0.0834	5.02	2.00-10.00
1.5	16.00(06)	20.95(13)	--	99	3.64	-1.09	58.05	0.0747	4.05	2.00-10.50
2.0	16.98(05)	22.01(16)	--	101	3.97	-1.98	69.70	0.0311	4.37	2.00-10.50
2.5	17.01(13)	21.88(17)	28.05(25)	110	7.19	-1.72	51.09	0.0423	3.92	2.00-10.50
Cu (II)										
0.0	16.74(11)	20.73(20)	25.98(26)	120	0.37	-1.88	72.44	0.0824	5.48	2.00-11.00
0.5	17.03(11)	21.92(21)	26.83(33)	117	1.66	-1.99	67.82	0.0225	3.98	2.50-10.70
1.0	16.84(16)	21.87(26)	26.95(39)	109	0.66	-1.74	98.92	0.0732	4.74	2.50-10.50
1.5	16.70(10)	--	26.81(20)	104	1.37	-1.88	69.97	0.0834	5.37	2.50-10.50
2.0	16.98(09)	--	27.44(26)	102	5.65	-1.41	77.32	0.0745	2.52	2.00-10.00
2.5	17.11(18)	22.93(31)	28.83(37)	114	3.33	-1.72	68.34	0.0958	3.55	2.00-10.50
Zn(II)										
0.0	10.93(06)	16.94(14)	29.82(28)	148	2.58	0.22	101.23	0.0813	6.20	2.00-11.00
0.5	10.73(11)	16.43(20)	29.64(30)	130	1.15	0.25	74.32	0.0201	2.24	2.00-10.50

1.0	10.94(13)	16.54(19)	29.73(32)	125	9.01	0.27	65.32	0.0010	2.27	2.00-10.50
1.5	11.75(16)	17.98(24)	--	120	1.36	0.94	77.82	0.0218	3.24	2.00-10.00
2.0	11.95(16)	17.78(26)	--	115	0.08	0.27	51.56	0.0417	2.02	2.00-10.00
2.5	12.00(20)	18.01(32)	30.08(40)	104	0.99	0.38	39.52	0.0319	4.34	2.00-10.50
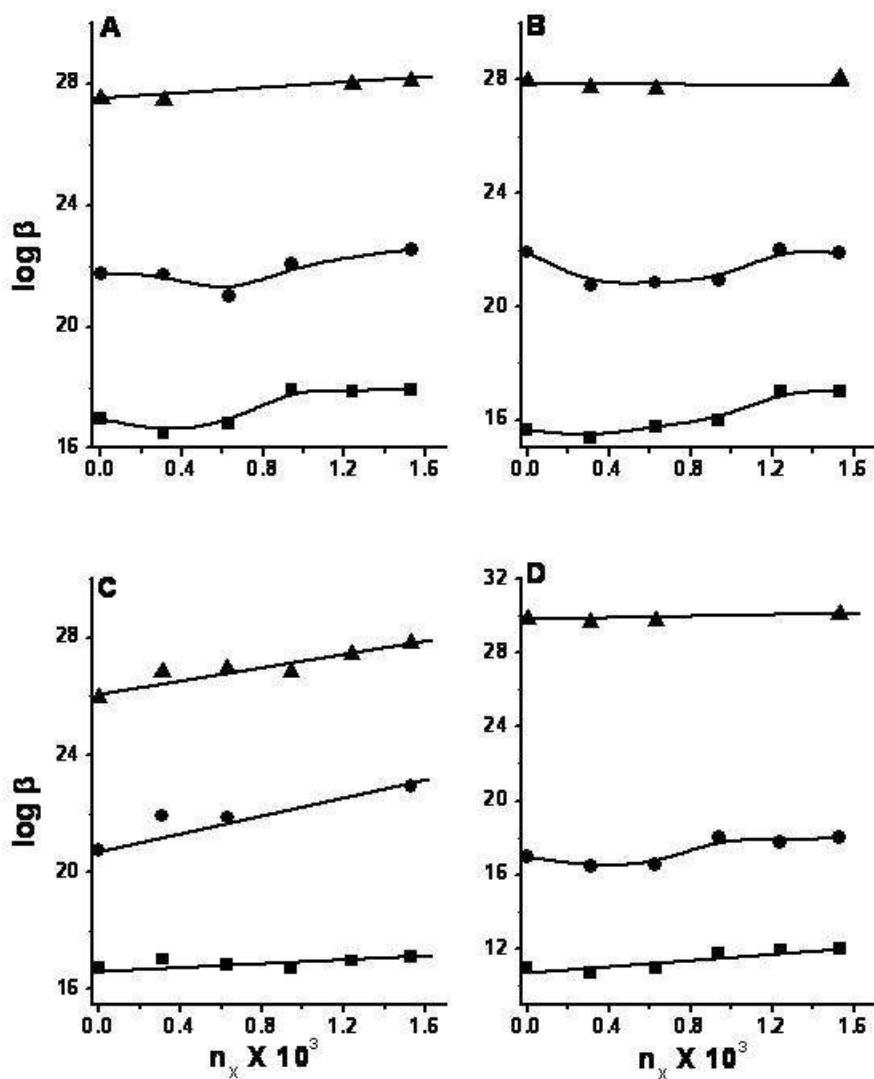
Figure 1: Variation of stability constant values of complexes with mole fraction of SLS (A) Co(II) B) Ni(II) C) Cu(II) and D) Zn(II) ((■) $\log\beta MLX$, (●) $\log\beta MLXH$, (▲) $\log\beta MLX_2H$
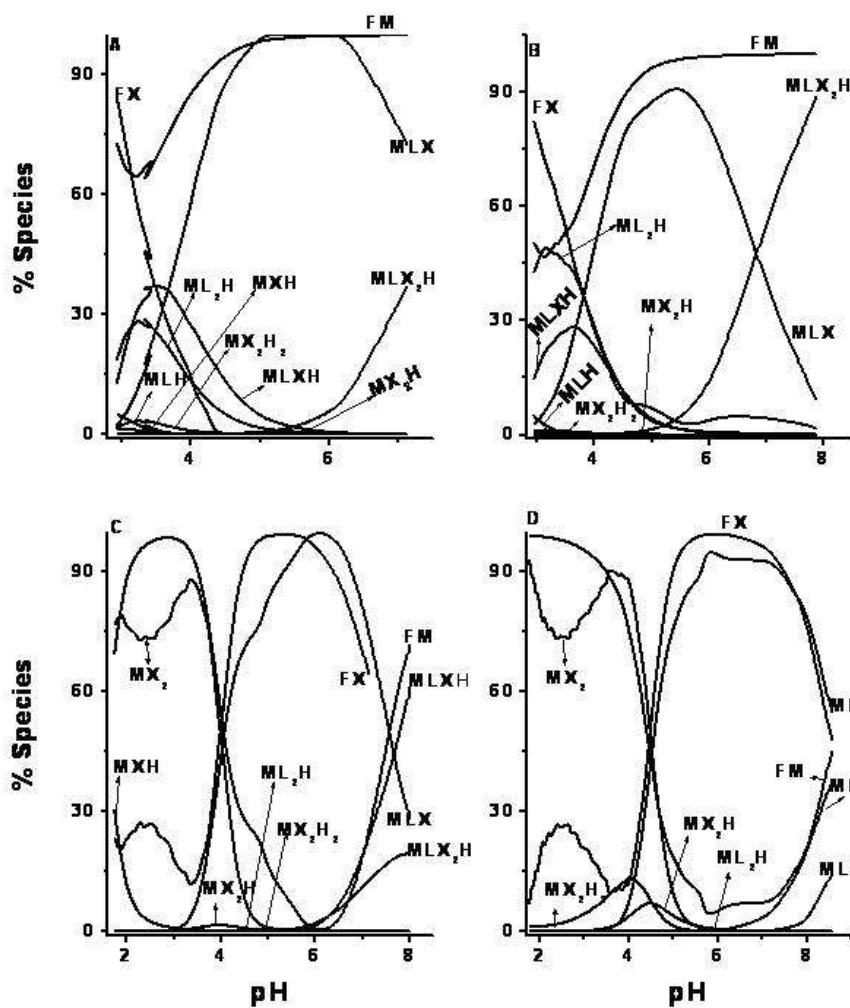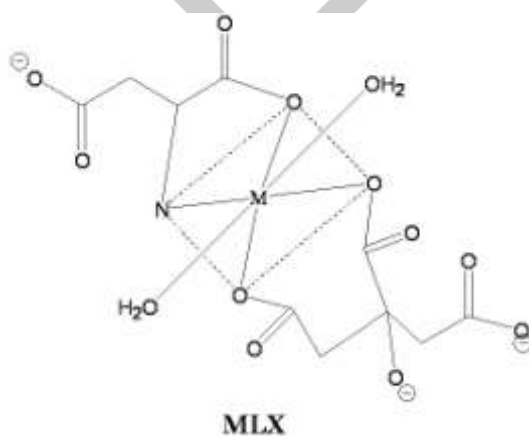
Figure 2: Distribution diagrams of ternary complexes of Asp-Cit in 2.0% w/v SLS water mixture. (A) Co (II), (B) Ni (II), (C) Cu(II) and (D) Zn(II)
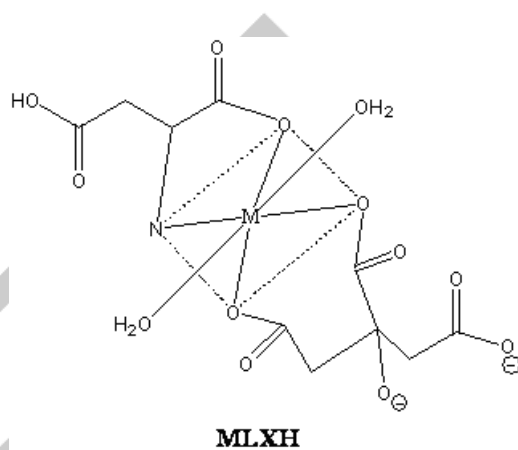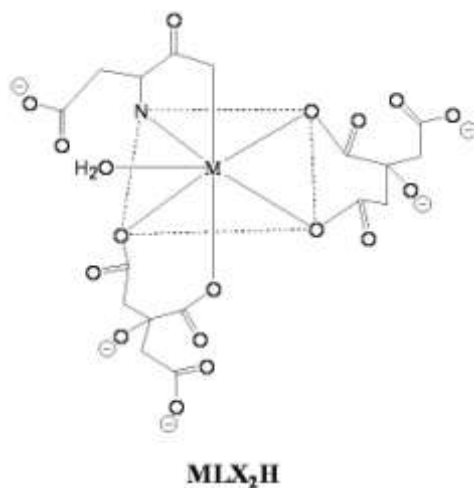

MLX

Figure 3: Plausible Structures of ternary complexes of L-aspartic acid (L) and Citric acid(X) with Co(II), Ni(II), Cu(II) and Zn(II)